



Electrochemical promotion of methane oxidation on Pd catalyst-electrodes deposited on Y₂O₃-stabilized-ZrO₂

C. Jiménez-Borja^a, S. Brosda^{b,*}, F. Matei^c, M. Makri^b, B. Delgado^a, F. Sapountzi^b, D. Ciuparu^c, F. Dorado^a, J.L. Valverde^a, C.G. Vayenas^b

^a Department of Chemical Engineering, (UCLM), Avda. Camilo José Cela 12, 13071 Ciudad Real, Spain

^b Department of Chemical Engineering, University of Patras, Caratheodory St 1, GR-26504 Patras, Greece

^c Faculty of Petroleum Refining and Petrochemistry, Petroleum-Gas University of Ploiesti, 39 Bucuresti Bd, 100680 Ploiesti, Romania

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Paper dedicated to Professor J.-M. Herrmann with sincerest respect and cordial wishes.

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ABSTRACT

The catalytic activity of Pd/YSZ and Pd-CeO₂/YSZ catalysts prepared via organometallic paste calcination or via wet impregnation has been investigated under conditions of excess in oxygen and at temperatures from 250 to 450 °C. The catalyst-electrodes were characterized via XRD, SEM, in situ electrical conductivity measurements, electrochemical current–potential curves and catalytic kinetic measurements. The impregnated Pd films were found to be more active with light-off temperatures of 270 °C vs. 320 °C for metal paste catalysts. Only the impregnated catalyst could be electropromoted at temperatures above 320 °C. The Pd-CeO₂/YSZ catalyst exhibited high catalytic activity but could not be electropromoted.

Co-feeding of ethylene or pre treatment in oxidizing ethylene–oxygen gas mixtures enhances the rate of methane conversion in comparison to non-treated samples and allows electrochemical promotion of the methane oxidation at temperatures as low as 320 °C. The reason for this behavior is discussed in view of detailed pre and post surface characterization and in situ electrochemical measurements.

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1. Introduction

Natural gas is forecasted to be used as an energy source for power plants and lean-burn natural gas vehicles in the future. The main component (85–95%) of natural gas is methane. The molecule of methane has the highest hydrogen to carbon ratio of all hydrocarbons and thus the combustion of methane yields the lowest amount of CO₂ per unit of produced energy [1,2]. Combustion of methane can be achieved through conventional flame combustion or via catalytic reaction. The main advantage of the catalytic process is the possibility, in principle, of obtaining complete oxidation of the fuel at much lower temperatures, with low fuel-to-air ratios while simultaneously controlling unburned hydrocarbons, CO and NO_x emissions. Among the noble metal catalysts, palladium has been widely reported as the catalyst of choice in methane combustion [3]. The dependence of the catalytic activity for methane combustion on the chemical state of palladium is quite complex. It is commonly accepted that at low temperature the active phase is crystalline PdO, which may exist in more than one form depending on the size of oxidized particles and on the type of the support, but at high temperature metallic Pd can also be active for methane

oxidation. Thus, it is desirable to have a significant amount of oxidized palladium present in the system [3].

Since the resistance of PdO is significantly higher than that of metallic Pd, it follows that in situ electrical conductivity measurements can be quite useful. The importance of such measurements with metal oxide catalysts has been demonstrated repeatedly by Herrmann and coauthors [4–8].

The catalytic activity of supported Pd can be strongly affected by the interaction with the support and support additives [1]. Ceria has been reported to be an effective support or additive to a support, such as Al₂O₃ and ZrO₂, for palladium catalysts. It can act as oxygen storage reservoir and thus can facilitate oxygen transport to Pd particles and therefore enhance the reoxidation process. Pure CeO₂ has poor thermal stability. Recently, it has been reported that the addition of zirconia (ZrO₂) to CeO₂ leads to an improvement of not only its oxygen storage capacity, redox properties and catalytic activity but also its resistance to high temperatures [3].

Y₂O₃-stabilized-ZrO₂ (YSZ), an excellent O^{2–} conductor, plays an increasingly important role in heterogeneous catalysis as nanodispersed catalyst carrier [9,10]. This solid electrolyte is the most common support for noble metal catalyst films to induce the effect of non-Faradaic electrochemical modification of catalytic activity (NEMCA) or electrochemical promotion of catalysis (EPOC) [11–17]. In such a NEMCA experiment the porous catalyst film deposited on YSZ serves as the working electrode. Its catalytic rate can be

* Corresponding author. Tel.: +30 2610962756; fax: +30 2610997269.
E-mail address: brosda@chemeng.upatras.gr (S. Brosda).

reversibly affected by externally applying a potential or current between the catalyst-working and the counter electrode [12]. Catalytic rates can be varied via electrochemical promotion by a factor of 100, while the induced steady-state change in catalytic rate can be up to five orders of magnitude larger than that anticipated rate of supply or removal of O^{2-} to the catalyst electrode [12].

The effect has been shown via several surface spectroscopic and electrochemical techniques [12] to be due to electrochemically controlled migration (backspillover) of promoting ionic species (O^{2-}) from the solid electrolyte to the metal gas interface. These backspillover ionic species form an overall neutral double layer at the metal/gas interface and affect catalytic rates by modifying the binding energy of chemisorbed reactants and intermediates via lateral electrostatic interactions [12].

The effect of current or potential on the catalytic activity is usually described by two parameters: the rate enhancement ratio (ρ), defined as [12]:

$$\rho = \frac{r}{r_0} \quad (1)$$

where r_0 is the catalytic rate at open circuit and r the catalytic rate under polarization and the apparent Faradaic efficiency, Λ , defined as [12]:

$$\Lambda = \frac{r - r_0}{I/2F} \quad (2)$$

where I is the applied current, F is the Faraday constant, and $I/2F$ equals the rate of O^{2-} supply to the catalyst.

Mixed ionic-electronic conductors, such as TiO_2 [18–21] and CeO_2 [22,23] can also be used to electrochemically promote catalyst films and it has been recently shown by Nicole et al. [24] that the phenomena of electrochemical promotion and metal-support interactions, including strong metal-support interactions (SMSI), are functionally identical and only operationally different [9,10,12,24], as they both stem from the migration of ionic species from the support to the metal/gas interface.

The electrochemically promoted deep oxidation of methane has been previously studied for Rh [25,26] and Pd catalyst-electrodes [23,27–29]. The catalytic activity of Pd catalysts prepared by organometallic paste deposition on YSZ can be significantly electro-promoted. It was found that the catalytic rate can be increased up to 70–90 times upon anodic polarization. In both previous studies on Pd [27,28] the reaction was carried out under near stoichiometric or slightly reducing conditions. Roche et al. [29] studied the electrochemical promotion of methane oxidation in excess of oxygen on sputtered Pd thin films deposited on YSZ and in the temperature range of 500–600 °C. At relatively high temperatures they found a catalytic rate increase of up to three. In a previous work [23] palladium films were prepared by wet impregnation technique and were deposited on YSZ and on CeO_2 interlayer on YSZ. Catalytic activity for methane oxidation in excess of oxygen was obtained only at temperatures higher than 550 °C. It was found that the catalytic activity of palladium can be further increased upon anodic polarization to 160%.

The aim of this study was to electrochemically promote the deep methane oxidation on Pd catalysts-electrodes under conditions of excess oxygen at low temperatures. For this purpose impregnated thin films of Pd deposited on YSZ or on a porous CeO_2 layer interfacing YSZ have been investigated in comparison to pasted Pd films.

2. Experimental

The solid electrolyte was a disk of 8 mol% Y_2O_3 -stabilized ZrO_2 (YSZ), of 19 mm diameter and 1 mm thickness (Henson Ceramics Limited). Inert gold counter and reference electrodes were deposited on one side of the solid electrolyte by application of thin

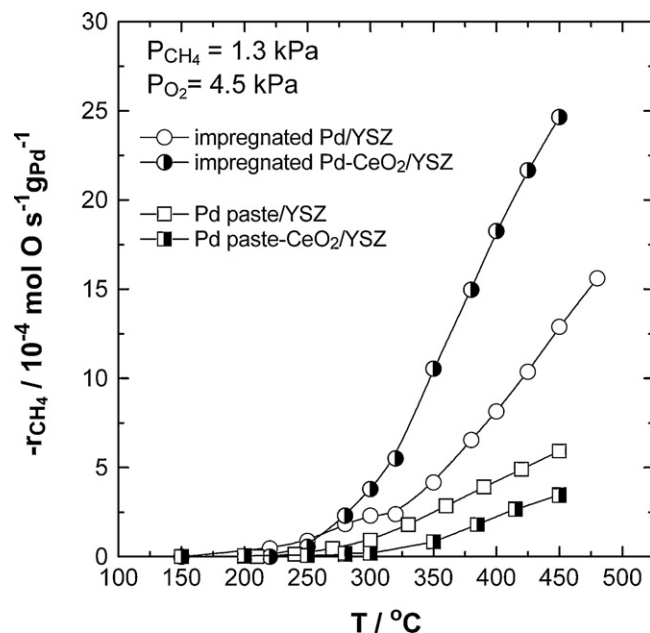


Fig. 1. Effect of reaction temperature on the catalytic (open circuit) methane consumption rate. Catalyst: impregnated Pd film. Experimental conditions: $P_{CH_4} = 1.3$ kPa and $P_{O_2} = 4.5$ kPa, $F_v = 200$ ml/min.

coatings of gold paste (Gwent Electronic Materials C1991025D2) followed by calcination at 800 °C for 2 h. The Pd catalytic film, serving also as the working electrode, was deposited on the other side of the disk, opposite to the counter electrode [12]. The geometric surface area of the working electrode was 2 cm² for all samples of this study.

Two catalyst-electrodes were examined, impregnated Pd on YSZ and impregnated Pd on CeO_2 /YSZ. For the preparation of the Pd- CeO_2 /YSZ catalyst, ceria was deposited on the area of the working electrode on the YSZ disk by impregnation, using a 0.1 M solution of $(NH_4)_2Ce(NO_3)_6$, followed by calcination at 600 °C for 2 h in order to achieve a CeO_2 loading of 1.72 mg.

The Pd films were deposited by impregnation technique on the YSZ disk for the Pd/YSZ catalysts, and on the CeO_2 layer applied on the YSZ disk for the Pd- CeO_2 /YSZ catalysts. Palladium films were prepared by successive steps of deposition and thermal decomposition of a palladium precursor solution. An aqueous solution of 0.1 M $[Pd(NH_3)_4](NO_3)_2$ (Sigma-Aldrich) was used as the precursor. Initially, 20 μ l of the precursor were applied on the YSZ or CeO_2 /YSZ substrate, using a plastic circular mask in order to obtain a 2 cm² geometric surface area of the catalytic film. Then, evaporation of the solvent took place at 100 °C for 10 min, followed by drying of the sample at 120 °C overnight and then calcination at 450 °C for 2 h. The procedure of successive steps of deposition, drying and heating was repeated until a final metal loading of 0.87 ± 0.01 mg Pd (total amount of 87 μ l precursor solution) for all impregnated samples was obtained.

Pd paste films deposited on the YSZ disk, and on the CeO_2 layer applied on the YSZ disk have been prepared by the application of thin coatings of an organic paste (Gwent Electronic Materials C 207 0604 D12). The films were dried at 120 °C overnight and calcinated in static air at 850 °C (5 °C/min) for 2 h. The final metal loading was measured by weighting the sample after calcinations and was 10 ± 2 mg Pd for all Pd paste samples.

The kinetic results have been expressed in mol O s⁻¹ g_{Pd}⁻¹ in all (Figs. 1, 2 and 5) both for paste and impregnated catalysts.

The crystalline phases of the palladium catalysts and its supports were examined by X-ray powder diffraction (XRD) performed in a PANalytical diffractometer equipped with a X'Celerator detector

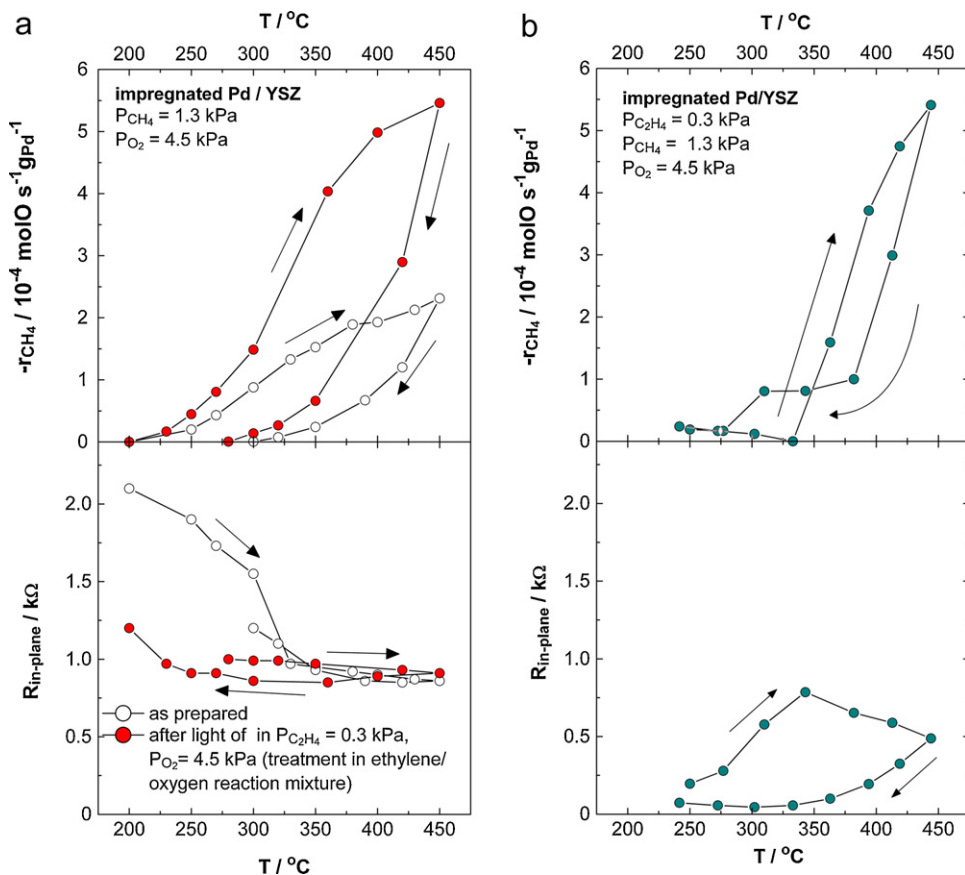


Fig. 2. Effect of temperature (top) on methane conversion rate and on in-plane resistance (bottom) of the catalyst-electrode Pd impregnated on YSZ (a) before and after treatment in a reactive gas mixture of ethylene and excess of oxygen and (b) by co-feeding of 0.3 kPa ethylene during light off. Catalyst: impregnated Pd film. Experimental conditions $P_{\text{CH}_4} = 1.3 \text{ kPa}$, $P_{\text{O}_2} = 4.5 \text{ kPa}$, $F = 200 \text{ ml/min}$, see text for discussion.

with monochromatic Cu K α 1 radiation ($\lambda = 1.54 \text{ \AA}$). XRD patterns were performed in the 2θ range between 20° and 90° , with a scan step size of 0.017 and 610.5 s per step. Rietveld refinement of the data was performed using the Fullprof Suite program.

Experiments were carried out in an atmospheric pressure single chamber quartz reactor with a volume of 30 cm^3 , as described in detail elsewhere [12]. Prior to the catalytic activity measurements, the samples were pre-treated under a gas mixture of $20\% \text{ O}_2$ diluted in helium at 300°C for 2 h.

Reactants were Messer–Griesheim certified standards of $5.6\% \text{ CH}_4$ in He, $10\% \text{ C}_2\text{H}_4$ in He and $20\% \text{ O}_2$ in He, and they could be further diluted in ultrapure (99.999%) He (L'Air Liquide). Gas flow rates were regulated using Brook mass flow controllers connected to a 4-channel Brose control box (model 5878). The total flow rate in all the experiments was $200 \text{ cm}^3 \text{ min}^{-1}$ (STP).

The reaction temperature was monitored via a K-type thermocouple placed inside the quartz tube, and controlled via a JUMO (iTRON 08) temperature controller.

Gas analysis of the reactants and products was performed using on-line gas-chromatography (Shimadzu A14), while an infrared analyzer (Rosemount Binios 100) was used for the continuous and quantitative measurement of the CO_2 concentration signal. The gas chromatograph utilizes a Thermal Conductivity Detector (TCD) equipped with two columns, a Molecular Sieve 5A (for the detection of O_2 , CH_4 and CO) and a Porapak Q column (for the detection of CH_4 , C_2H_4 and CO_2). TCD signals were integrated and recorded on line by the use of a Hewlett Packard integrator (model 3395).

The contributions of homogeneous reaction as well as the catalytic rate of methane or ethylene combustion on both the pure solid electrolyte and gold electrodes were found to be negligible

under operating conditions. Thus, all the catalytic activity should be exclusively attributed to palladium. Carbon dioxide was the only C-containing product since CO and other carbon based compounds were not detected.

During catalytic activity measurements the in-plane resistance of the catalyst film was obtained. For this purpose the catalyst-electrode (working electrode) was connected to two point contacts (Au wires) in a distance of 8 mm from each other. The Ohmic resistance between these two points was obtained with a Digital Multimeter (Mastech MY-68) during light off experiments and only under open circuit conditions.

Application of constant currents or potentials was carried out using an SOLARTRON electrochemical interface 1255.

3. Results and discussion

3.1. Catalytic activity

The effect of temperature on methane oxidation was studied under atmospheric pressure and steady-state conditions in the temperature range of 120 – 450°C with an inlet gas composition of $1.3\% \text{ CH}_4$ and $4.5\% \text{ O}_2$. Fig. 1 shows, that the catalytic activity, expressed in methane conversion rate per gram Pd catalyst, is significantly affected by the preparation technique of the Pd film and by the presence or absence of a CeO_2 interlayer. Impregnated Pd on YSZ is more active than the paste catalyst-electrode. The onset of catalytic CH_4 oxidation with $2 \times 10^{-4} \text{ mol O s}^{-1} \text{ g}_{\text{Pd}}^{-1}$ is observed at 270°C for impregnated samples in comparison to 320°C for paste Pd films. Methane conversion rate is found $7 \times 10^{-4} \text{ mol O s}^{-1} \text{ g}_{\text{Pd}}^{-1}$ at 400°C for impregnated Pd on YSZ vs.

$3 \times 10^{-4} \text{ mol O s}^{-1} \text{ g}_{\text{Pd}}^{-1}$ at for paste films. The CeO_2 layer was found to further enhance the open circuit activity of impregnated Pd on YSZ to $18 \times 10^{-4} \text{ mol O s}^{-1} \text{ g}_{\text{Pd}}^{-1}$ at 400°C (Fig. 1). The paste Pd films with and without CeO_2 interlayer are much less catalytically active. The high catalytic activity of impregnated Pd in presence of ceria can be explained partially by the higher dispersion achieved on the porous and thus rough ceria interlayer. Further, the CeO_2 facilitates a strong improvement of the oxygen storage capacity and this leads to a substantial stabilization of the PdO phase, which is essential for the low temperature methane combustion [3].

Pd catalysts dispersed on YSZ exhibit excellent catalytic performance in ethylene oxidation with TOF approaching 50 s^{-1} [30]. This led to the idea of co-feeding small amounts of ethylene to an overall oxidizing methane/oxygen reaction mixture in order to ignite methane oxidation at lower temperatures and to increase the open and closed circuit catalytic performance of Pd films deposited on YSZ. Preliminary, unpublished studies have revealed that indeed the methane consumption rate of impregnated Pd films on YSZ can be significantly improved with this approach, and that electrochemical promotion in excess of oxygen is possible at temperatures as low as 320°C . Furthermore, it has been found, that the in-plane resistance of the Pd film changes dramatically with temperature and gaseous composition even if excess of oxygen is sustained. The effect of ethylene on the catalytic performance of impregnated Pd films has been therefore investigated in more detail by comparing the following two approaches (Fig. 2):

- (1) A set of light off curves in the temperature range of $150\text{--}450^\circ\text{C}$ and in the sequence
 - a. CH_4/O_2
 - b. $\text{C}_2\text{H}_4/\text{O}_2$ Pre-treatment
 - c. CH_4/O_2
 has been carried out (Fig. 2a). CO_2 formation rate, methane conversion and in-plane resistance were recorded in situ.
- (2) Light off curve in the temperature range of $150\text{--}450^\circ\text{C}$ in an oxidizing reaction mixture of ethylene, methane and oxygen (Co-feeding of small amounts of ethylene to the methane-oxygen reaction mixture, Fig. 2b).

Fig. 2 shows the dependence of the catalytic rate of methane consumption on the reaction temperature for these two approaches. Two fresh samples of impregnated Pd with equal amount (0.87 mg) have been used. The treatment with a reactive $\text{C}_2\text{H}_4/\text{O}_2$ feed or the presence of C_2H_4 in the CH_4/O_2 feed for the improvement of methane oxidation is significant in both approaches. The ignition temperature for methane combustion is decreased and the conversion for a given temperature is increased. In both experiments, the temperature dependence of methane conversion and to some extent of the in-plane resistance too, shows a significant hysteresis.

PdO forms between 300 and 400°C and is stable in air and at atmospheric pressure up to 800°C . Once PdO is decomposed, temperatures well below 650°C are needed for the reoxidation of Pd [31], thus leading to a hysteresis in methane conversion as a function of temperature. PdO dispersed catalysts on ZrO_2 show a significant decrease in the transformation temperature ($>100^\circ\text{C}$) from PdO to Pd⁰ [32]. Surprisingly, this pronounced hysteresis (Fig. 2) is observed although the catalyst in this study has not been exposed to temperatures higher than 450°C and its regeneration should be out of concern. In a recent study [33] controlled chemical reduction with pulsed methane into the reaction mixture was investigated on Pd/ $\text{CeO}_2\text{--ZrO}_2$ catalysts. The degree of reduction plays an important role since slight reduction improves the catalytic activity in comparison to either fully oxidized or fully reduced catalysts. The treatment with a reactive $\text{C}_2\text{H}_4/\text{O}_2$ feed or

the presence of C_2H_4 in the CH_4/O_2 feed (Fig. 2a and b), respectively, decreases the in-plane resistance of the Pd film at identical reaction temperature. Thus one may conclude that PdO is partially reduced to metallic Pd by taking into account, that PdO shows much higher bulk and surface resistance than Pd⁰ [34].

In a recent study by Garcia Fierro and co-workers [35] $\text{C}_2\text{--C}_4$ hydrocarbons (C_2H_6 , C_3H_8 and $n\text{-C}_4\text{H}_{10}$) have been successfully used to promote methane oxidation on Pt/ $\gamma\text{-Al}_2\text{O}_3$ dispersed catalysts. They explain their findings in view of the exothermic reaction of higher alkanes which initiate at much lower temperatures than methane combustion. The rate determining step in methane combustion is considered to be the abstraction of the first hydrogen from the adsorbed methane molecule [36,37]. Thus the heat locally generated at active sites during alkane oxidation is may be used to reach the activation energy of this rate limiting step. The author's second possible explanation is based on the kinetics in methane oxidation on noble metals which is positive order with respect to methane and positive order with respect to oxygen only under fuel rich conditions. The latter is changing to near zero or even negative order reaction kinetics if fuel lean conditions are used [28,30, 31 and references here in]. Oxygen thus inhibits the reaction at full coverage. Co-feeding of alkanes may lower the coverage of oxygen and this cleavage of the surface leads to free and active surface sites for methane adsorption.

3.2. Pre and post experiment characterization of the Pd catalysts

Fig. 3 shows the XRD pattern of impregnated Pd catalyst deposited directly on YSZ (Fig. 3a) and deposited on a ceria layer (Fig. 3b). For both catalysts, XRD spectra of the fresh (Pd film as prepared) and used sample (Pd film after exposure to reaction conditions) are compared. The following peaks correspond to the palladium phases:

- (i) Metallic palladium consistent with a face-centred cubic (fcc) structure where reflections appear at 40.1° , 46.6° , 68.1° and 82.1° corresponding, respectively, to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of Pd⁰ (JCPDS-ICDD Card No. 05-0681 [38]).
- (ii) Palladium oxide consistent with a tetragonal structure where reflections appear at 33.8° and 54.7° corresponding, respectively, to the (1 0 1) and (1 1 1) planes of PdO (JCPDS-ICDD Card No. 41-1107 [38]).

The solid electrolyte shows the characteristic peaks of YSZ, $\text{Zr}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}$ corresponding, to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes (JCPDS-ICDD Card No. 01-082-1246 [38]). CeO_2 is characterized by the main peak at 28.5° , corresponding to the (1 1 1) plane of face-centred cubic cerium oxide (JCPDS-ICDD Card No. 34-0394 [38]).

The fresh samples of impregnated Pd on YSZ and on CeO_2/YSZ show only reflections of palladium oxide. After exposure to reaction conditions, which have been chosen to be always of excess in oxygen, the impregnated Pd on YSZ exhibits only the metallic phase while impregnated Pd on CeO_2/YSZ stabilizes both phases the metallic Pd and palladium oxide.

Table 1 summarizes results of the Rietveld treatment of the XRD analysis. The CeO_2 layer does not show a clear trend in the crystallite size comparing fresh samples (14 vs. 21 nm) and used samples (29 vs. 30 nm). On the other hand, CeO_2 affects clearly the crystallite size of PdO and CeO_2 before and after experiment. For both, PdO and CeO_2 , the average crystallite size decreases significantly from 21 to 11 nm and 23 to 10 nm, respectively. This is unexpected and can be understood only by considering the phase changes from PdO (fresh sample) to both, metallic Pd and Pd oxide (used sample).

The catalytic activity of impregnated Pd on CeO_2/YSZ was the best among the catalyst-electrodes studied. Only in this case the

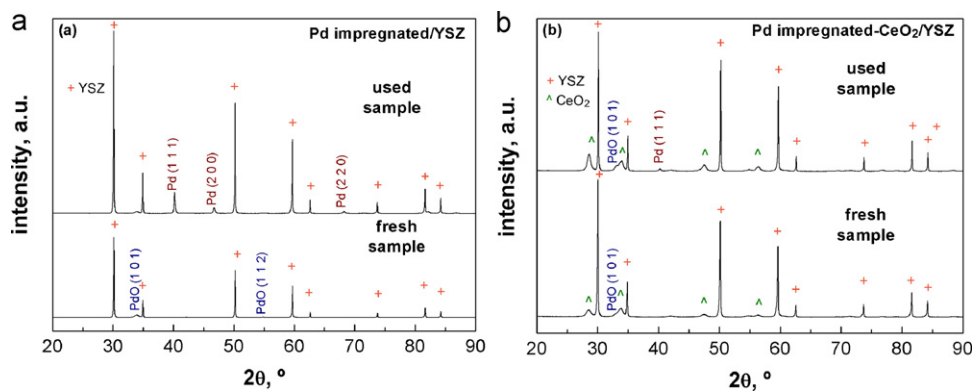


Fig. 3. XRD spectra for the catalyst-electrodes (a) Pd impregnated on YSZ and (b) Pd impregnated-CeO₂ on YSZ before and after exposure to reaction conditions.

PdO phase was present. In several studies it has been concluded that this is the major requirement for high methane combustion rates at medium temperatures, i.e. 200–500 °C [31,33].

The structure and morphology characterization of the different catalytic layers was carried by scanning electron microscopy (SEM) using a JEOL 6490LV microscope. SEM pictures from the cross section of impregnated Pd on YSZ and on CeO₂/YSZ are shown in Fig. 4. The catalytic films exhibit excellent adherence on the electrolyte and their porosity is good enough to facilitate migration of O^{δ-} promoter species from the solid electrolyte to the catalytic film during NEMCA experiments [12]. The thickness of the palladium film is less than 5 μm.

3.3. Electrochemically promoted methane oxidation

Pd paste electrodes have not been investigated for electrochemical promotion experiments since their open circuit catalytic activity was very small in excess of oxygen and at temperatures below 400 °C.

The catalytic activity of the impregnated Pd/YSZ and impregnated Pd-CeO₂/YSZ catalysts under polarization was investigated in the temperature range of 320–450 °C.

It was found that the catalytic activity of the catalyst Pd-CeO₂/YSZ cannot be electropromoted, i.e. application of anodic or cathodic potentials do not change the methane combustion rate. From a practical viewpoint it is obvious that the extent of thermal migration of promoting species, O^{δ-}, from the support, here the CeO₂ interlayer, matches the migration of the electrochemically controlled promoting species which is responsible for the NEMCA effect. Furthermore, electrochemically promoted methane oxidation was found on the non-treated Pd film (Fig. 2a, open symbols) only at 450 °C and with relatively high overpotentials, i.e. $U_{WR} > 1$ V. The co-feeding of ethylene or the treatment in C₂H₄/O₂-rich gas mixture is an essential requirement to achieve electrochemical promotion of methane oxidation in excess of oxygen and at lower temperatures. Previous results obtained on Pd films deposited on YSZ [23,29] allowed for electrochemically promoted CH₄

combustion only at temperatures higher than 550 °C at which partial reduction of PdO is expected.

Fig. 5 shows two typical galvanostatic NEMCA experiments for an impregnated Pd film which has been exposed to a reactive C₂H₄/O₂ mixture prior to the transients. It shows the transient effect of constant positive current application on the rates of CO₂ formation and on the catalyst potential U_{WR} . The experiment was carried out at fixed feed gas composition, $P_{O_2} = 4$ kPa, $P_{CH_4} = 1.3$ kPa at 350 °C (Fig. 5a) and 400 °C (Fig. 5b). Initially, for $t < 0$, the circuit is open and the steady-state rates of CH₄ oxidation to CO₂ is equal to 2.1×10^{-7} mol O/s (Fig. 5a). At $t = 0$, a constant anodic current, ($I = 300 \mu A$) is applied between the catalyst and the counter electrode. Oxygen ions, O²⁻, are transferred from the YSZ support to the Pd catalyst-electrode at a rate $I/2F$ equal to 1.55×10^{-9} mol O/s, where F is the Faraday constant. At the same time the rate of CH₄ oxidation to CO₂ increases and after 10 min approaches a new steady state ($r = 2.5 \times 10^{-7}$ mol O/s). The increase in the catalytic rate $\Delta r (=0.4 \times 10^{-7}$ mol O/s) is 25 times larger than the rate of ion transport, $I/2F$. This implies that each O²⁻ supplied to the Pd catalyst surface causes on average 25 chemisorbed O atoms to react with methane and form CO₂ and H₂O. The rate enhancement ($\rho = 1.18$) is rather small, and increases only slightly to 1.7 for 400 °C (Fig. 5b). After current interruption, the catalytic rate of CO₂ formation returns to its initial open circuit (ocp) value showing the reversibility of the phenomenon. It is interesting to examine the second transient obtained at 400 °C (Fig. 5b), in which the rate under closed circuit conditions does not reach a stable steady state value even after more than 60 min of constant polarization. The observed behavior at 400 °C may be due to the onset of subsurface oxidation of the Pd sample.

In a previous study on a Pd/YSZ [23] a clear permanent promotional effect was found after the current was interrupted. This was attributed to PdO formation during anodic polarization. In that study in comparison to ours, a significant higher working temperature of >550 °C was used since at lower temperature electrochemical promotion was not observed. It is well known [32] that the phase transformation of PdO to metallic Pd takes place between 600 and 700 °C when Pd is deposited on ZrO₂, and thus similar reduction behavior is to be expected when yttria-stabilized zirconia is used as support. Thus a higher percentage of metallic palladium is available at open circuit conditions than in the present study, which is gradually oxidized during the application of an anodic current or potential. Current interruption does not lead to a reversible change to the original open circuit rate since sub-surfaces or even bulk PdO is not reduced spontaneously.

Fig. 6 shows the steady state effect of temperature and of catalyst potential on current, Tafel plots, (Fig. 6a), on the rate enhancement ratio (Fig. 6b) and on the Faradaic efficiency (Fig. 6c). The catalyst potential was varied from –600 mV (cathodic polarization)

Table 1
Average crystallite size from Rietveld treatment.

	Impregnated Pd/YSZ	Impregnated Pd-CeO ₂ /YSZ
Fresh samples	No Pd PdO 14 nm	No Pd PdO 21 nm CeO ₂ 23 nm
Used samples	Pd 29 nm No PdO	Pd 30 nm PdO 11 nm CeO ₂ 10 nm

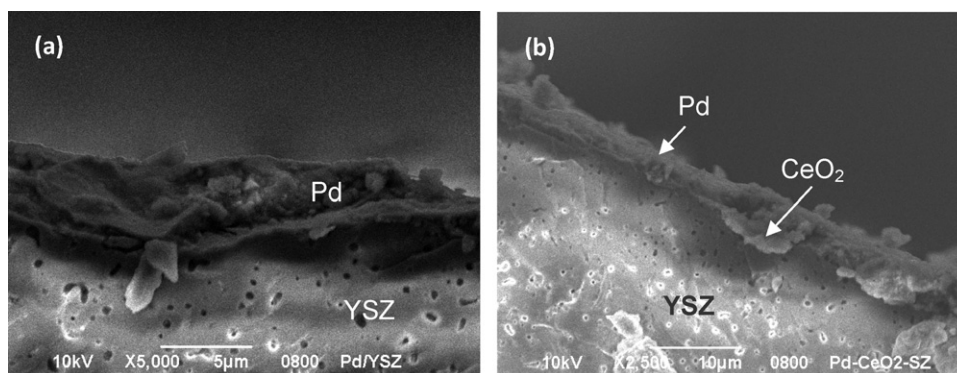


Fig. 4. SEM pictures from the cross section of the catalyst-electrodes (a) impregnated Pd on YSZ and (b) impregnated Pd-CeO₂ on YSZ.

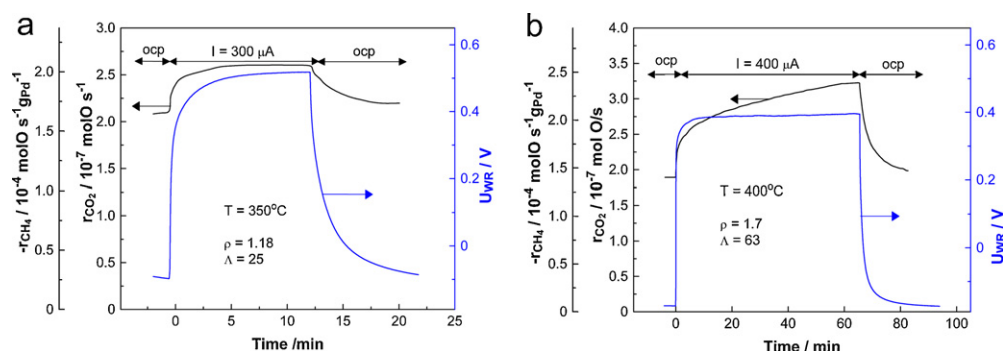


Fig. 5. Transient response of the catalytic CO₂ formation rate, r_{CO_2} , the methane consumption rate, $-r_{\text{CH}_4}$, and of the catalyst potential upon application of (a) $I = 300 \mu\text{A}$ at 350 °C and (b) $I = 400 \mu\text{A}$ at 400 °C. Catalyst: pre-treated impregnated Pd film. Experimental conditions $P_{\text{CH}_4} = 1.3 \text{ kPa}$, $P_{\text{O}_2} = 4.5 \text{ kPa}$, $F = 200 \text{ ml/min}$.

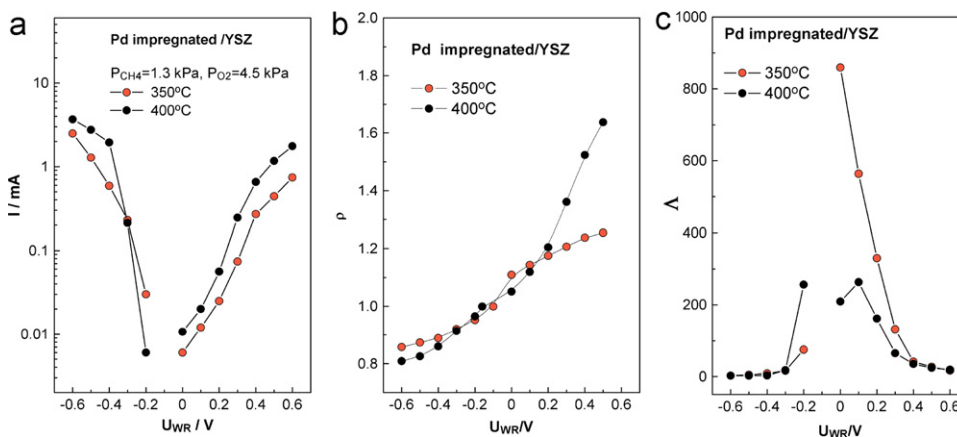


Fig. 6. Effect of applied potential and temperature on the electrochemically promoted methane oxidation on Pd impregnated/YSZ catalyst-electrode. (a) Tafel plots, (b) effect of applied potential on the rate enhancement ratio, ρ , (c) effect of applied potential on the Faradaic efficiency, Λ . Catalyst: pre-treated impregnated Pd film. Experimental conditions: $P_{\text{CH}_4} = 1.3 \text{ kPa}$, $P_{\text{O}_2} = 4.5 \text{ kPa}$, $F = 200 \text{ ml/min}$.

to +600 mV (anodic polarization). One observes that the reaction exhibit a pronounced electrophobic behavior [12,28] that is the rate of CH₄ oxidation increases significantly, up to 100% with positive potential. At 350 °C Faradaic efficiency, Λ , values as high as 800 are obtained.

At low oxygen inlet partial pressures (and consequently low coverage) an anodic polarisation reduces the binding strength of oxygen on the catalyst surface, thus leading to a more active adsorbed oxygen species which enhances the rate of methane oxidation [12,28]. At high inlet oxygen partial pressures, as is the case in this study, the oxygen coverage is high, the Pd active sites are occupied almost completely by oxygen and surface PdO is formed at the expense of surface Pd⁰ species. This is apparently the reason

why in excess of oxygen the electrochemical promotion effect is smaller, since anodic polarisation of the Pd film is not sufficient to decompose partially the surface PdO.

4. Conclusion

The aim of the present study was to achieve electrochemical promotion of the methane oxidation over palladium catalyst under conditions of excess oxygen and at low temperatures. At these temperatures methane oxidation is slow. However Pd catalysts dispersed on YSZ exhibit excellent catalytic performance in ethylene oxidation with TOF approaching 50 s⁻¹ [17]. This led to the idea of co-feeding small amounts of ethylene to an

overall oxidizing methane/oxygen reaction mixture in order to activate the methane oxidation at lower temperatures and to increase the open and closed circuit catalytic performance of Pd films deposited on YSZ.

The present study has revealed that the methane consumption rate of impregnated Pd films on YSZ can be significantly improved when small concentrations of ethylene (~ 0.3 kPa) are cofed to the reaction mixture. In this way it was shown that electrochemical promotion can affect the catalytic oxidation of methane, even in excess of oxygen and at low temperature ($>320^\circ\text{C}$). The rate of methane oxidation is enhanced with positive potentials. The rate enhancement ratio, ρ , for CH_4 consumption is rather small with ρ values up to 2 but with apparent Faradaic efficiencies exceeding 500.

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